AD-A166 745 CHEMICALLY CROSS-LINKED HEAT-SHRINKABLE POLYETHYLENE TUBES(U) FOREIGN TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH I MIHALCEA ET AL. 10 APR 86 FTD-ID(RS)T-0480-85 1/1

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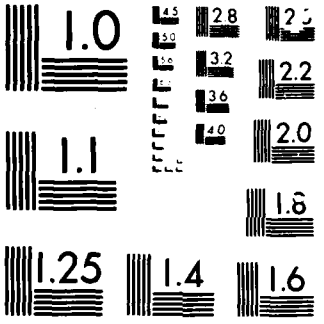

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by

Ion Mihalcea, Silviu Jipa, et al.

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HUMAN TRANSLATION

FTD-ID(RS)T-0480-85 10 April 1986

MICROFICHE NR: FTD-86-C-001709

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English pages: 9

Source: Materiale Plastice, Vol. 20, Nr. 2, April-June 1983, pp. 113-116

Country of origin: Romania
Translated by: SCITRAN
F33657-84-D-0165
Requester: FTD/TQTR

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WPAFB, OHIO

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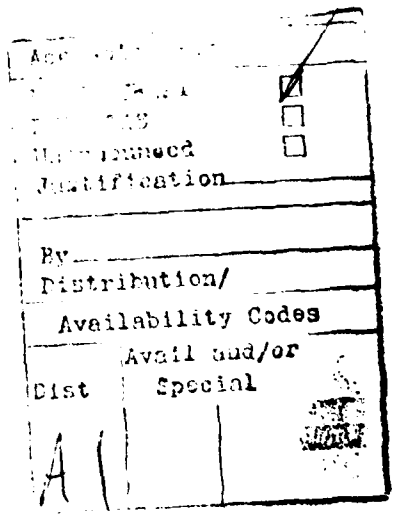

CHEMICALLY CROSS-LINKED HEAT-SHRINKABLE POLYETHYLENE TUBES

Ion Mihalcea, Silviu Jipa, Sorin Ilie, Constantin Cazac,
Vlaicu Contineanu and Mihai Zaplaic

The memory effect of heat-shrinkable tubes made of low density polyethylene obtained by irradiation with accelerated electrons is presented. The dependence of the cross-linked polyethylene contraction force on time, temperature, degree of cross-linking, etc., is emphasized.

Some mechanical, electrical and chemical properties of the irradiated polyethylene are evident. (also abstracts in Romanian and Russian).

Within the temperature range where the polymers have a thermoelastic behavior, their imprinted deformations lead to macromolecular orientations. These orientations stay after cooling, hence strong inner tension occurs. Through heat, the polymer tends to relax which cancels almost entirely the previous imprinted deformations. This feature is known as plastic materials' memory. The memory phenomenon has been noticed with a large number of polymers such as polyethylene; polypropylene; vinyl-poly-chloride; vinyliden-poly-fluoride; poly-tetra-fluor ethylene; polyurethene; ethylene copolymers with vinyl-acetate, with ethyl-acrylate and with butanyene; neoprene rubber; fluoride rubber; silicone rubber, etc. [1-8].

The experiment shows that the memory effect grows stronger with the increasing number of cross-linkings in the polymer. In order to obtain heat-shrinkable polyethylene items, the best reticulation range should be between 40-60% [3-6]. These items found extensive use in the most diversified fields: electro-technics, electronics, mining industry, civil and industrial construction, agriculture, etc. [8-10].

Their usefulness is due to both the higher functional features of some parts of the system and to an improvement of engineering esthetics.

The aim of this work is finding technological parameters to produce heat-shrinkable cross-linked polyethylene tubes using accelerated electrons irradiation.

The experimental procedure

We have manufactured the tubes out of low density polyethylene with anti-oxydant ingredients and for some samples also with fire-proof agents. We have studied 9 tube sizes with inner diameters between 1.4 and 11.6 mm and wall thicknesses between 0.45 and 1.7 mm.

For cross-linking purposes, the irradiation of the tubes has been performed using a Van de Graaf accelerator in a scanning electron flux of 0.6 MeV; a current intensity 100 μa; a conveying device was used to bring the tubes in the electron flux, its irradiating geometry being shaped as a figure 8. The tubes made one simple crossing which makes up for six passes on both sides.

For an evaluation of the radiation dose distribution throughout the tubes, we used a method of simulating the tubes' wall thickness by a tri-cellulose acetate (TAC) film. The light transmission through the irradiated samples from opposite directions and perpendicular to the scanning plan has been measured with a spectral photometer "SPECTRONOM 204" having in mind the radial distribution of the dose. We used the calorimetric method for the TAC film calibration.

The amount of reticulation was measured by the method of oxylene extraction after 20 hours boiling, also by elongation method at 150° celsius, 15 minutes, under a 20 N/ cm^2 stress.

The tubes have been drawn pneumatically and glycerine was used as a heating medium.

The factors influencing the tubes heat shrinkage are: time, temperature and thermo-contraction force. For the thermo-contraction time measurement, we used a simple device shown in Figure 1.

The thermo-contraction force measurement was made with a force captator tuned to the range 0-10 N, working in a tensiometric bridge as in Figure 2. The captator is made out of OLC-45 steel and has two tensiometric markings type 6/120 LV-11 applied with an adhesive resistant up to 250° celsius. For measurements, a Hottinger Baldwin Messtechnik KWS/T-5 bridge has been used. The captator, connected with the tensiometric bridge, was calibrated under stress for each contraction temperature studied.

We used the following parameters to express the experiment

$$S\,(\%) = \frac{D_e - D_t}{D_e} \cdot 100$$

$$R\,(\%) = \frac{D_e - D_t}{D_e - D_0} \cdot 100$$

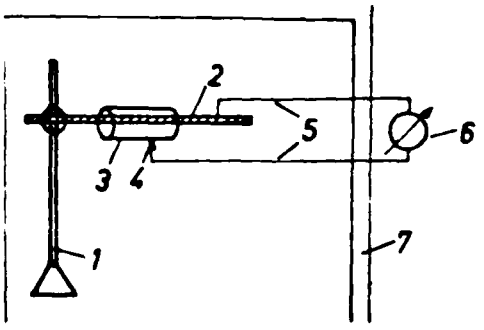

Figure 1. General layout of the wiring ion force contraction time evaluation: 1--glass stand; 2--brass rod; 3--thermo-contractable tube; 4--contactor; 5--insulated wires; 6--ohmmeter; 7--furnace

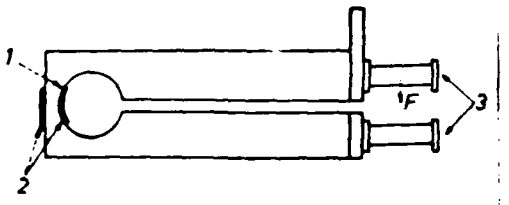

Figure 2. The force captator scheme.
1--active part; 2--tensiometric markings; 3--sample's resting ends for the contraction force

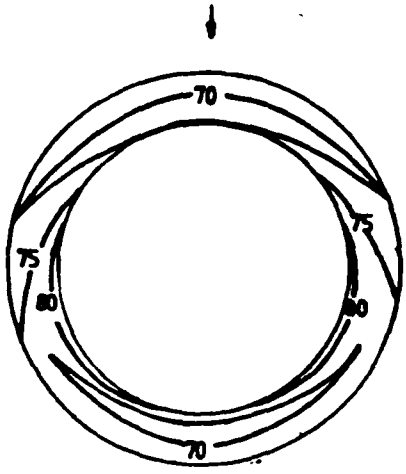

Figure 3. Isodose curves recorded while irradiating a polyethylene tube having the following dimensions: Φ_{ext}=4.5 mm; Φ_{int}=3.2 mm; wall thickness = 0.65 mm

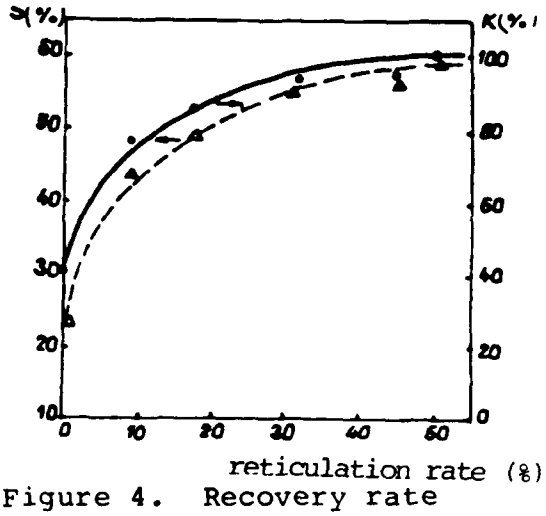

Figure 4. Recovery rate variation (R) and contraction rate (S) with the rate of reticulation. Contraction temperature 140° celsius; contraction time: 8 mins. Where: S = the thermocontraction rate
R = recovery rate
D_ε = drawn tube diameter;
D_t = tube's diameter contraction at "t" temperature
D_o = initial tube's diameter

RESULTS AND DISCUSSION

The irradiation evenness of the tubes ought to be the principal factor in the radiochemical technology for heat-shrinkable tubes production. For verifying the irradiation evenness, we computed isodose curves in tube walls with a thickness between 0.65 and 1.7 mm. Figure 3 shows the isodose curves for a 0.65 mm thick tube irradiated with 0.6 MeV energy electrons. In this instance, the maximum dose variation is under 30% throughout the wall thickness. For tubes with a wall thickness of 1.7 mm, the dose variations reached up to 80% from maximum recorded value, which demonstrates the fact that in this particular instance the 0.6 MeV energy was insufficient. From the isodose studied for wall thicknesses under 1.4 mm, we could assess that the 0.6 MeV energy is enough. The less the wall thickness, the more evenness of the dose. This fact is due to the electrons emerging from the first wall and then dissipating their energy surplus in the first strata of material of the inner surface of the tube along the irradiation direction.

About a 20% increase of dose evenness occurs also on the inner lateral tube surface and this is probably due to the primary electron flux scattered in the tube thickness.

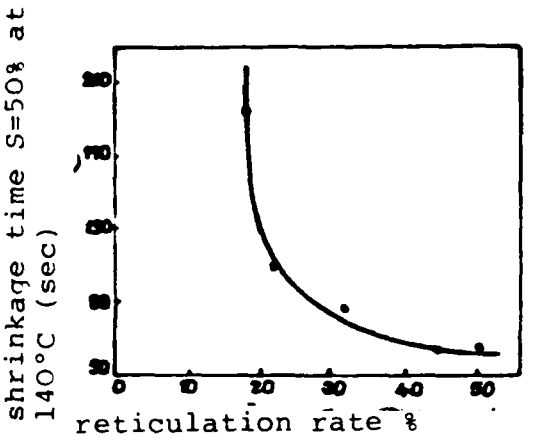

Figure 5. Heat shrinkage time variation for S = 50% and 140° celsius versus reticulation

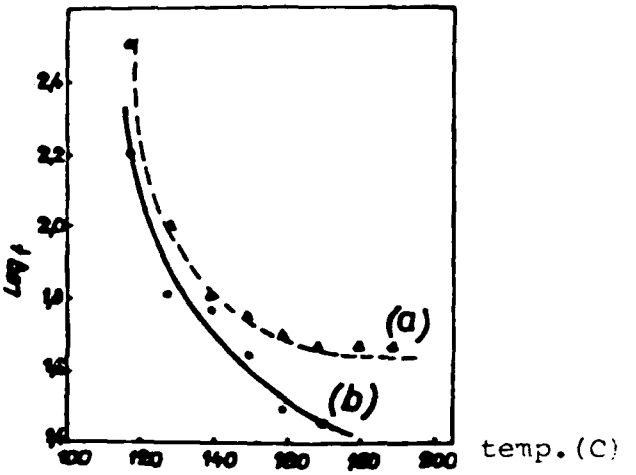

Figure 6. Heat shrinkage time variation for S=50% versus temperature (cross-linking rate 45%). a--polyethylene tube, fireproofed and with anti-oxidization additive. b--polyethylene tube with anti-oxidization additive

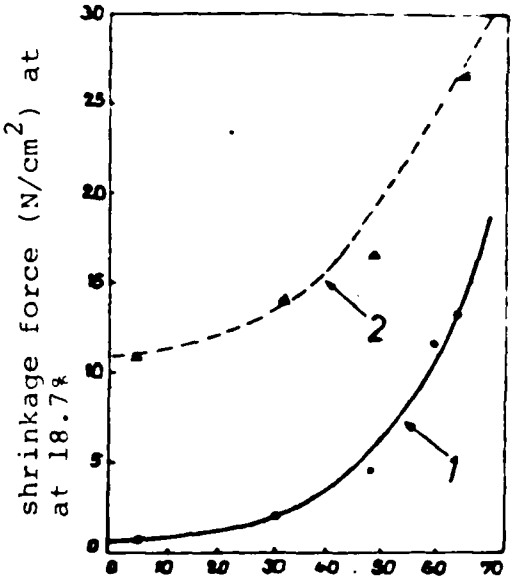

Figure 7. Contraction force variation while sample is heated at open flame (1) and after cooling at 20°C (2) for S=18.7% versus cross-linkage rate

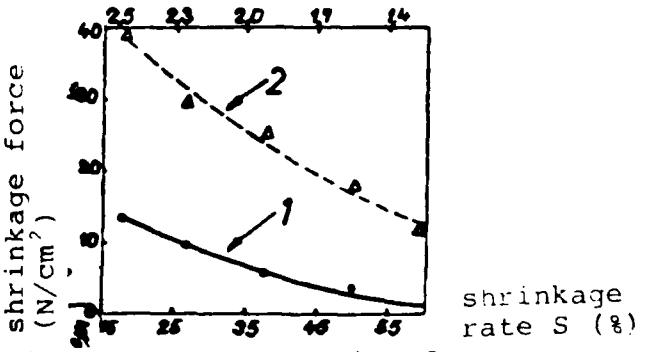

Figure 8. Contraction force variations versus contraction rate while sample is heated at open flame (1) and after cooling at 20°C (λ)

cross-linkage rate, %	Heat shrinkage force (N/cm^2 for a shrinkage rate of 34.5%, heated at open flame	heated at 140°C	cooling at 20°C
0	0	0	0
0,23	0	0	5,76
11,36	0,25	0,29	10,55
20,96	0,61	0,77	11,99
34,96	1,83	2,26	16,21
47,14	5,60	7,23	20,60
49,87	8,99	9,01	21,68

TABLE 1. Heat-shrinkage force variation with cross-linking rate during shrinkage at flame, at 140°C and after cooling.

characteristic	value	characteristic	value
resistivity, kV/mm	25	lengthwise modification, %	10
permitivity at 20°C and 1 MHz	2.0	forced heat-shrinkage:	no cracks
volume resistivity ohm.cm.min.	10^{14}	corrosiveness	none
withstanding heat shock (4 hrs. at 200°C)	no cracks no leaks	tensile strength, kgf/cm^2	175
water absorption (24 hrs. at 24°C)	0.05	elongation up to breaking point, %	400

TABLE 2. Electrical and mechanical features of heat-shrinkable tubes studied.

Among the heat-shrinkage features we studied was that of the recovery variation (R) and shrinkage (S) versus cross-linking rate. Figure 4 shows this interaction when one considers tube samples drawn 2.5:1. We can see that the memory effect of the polyethylene tube is dependent of the polymer's cross-linking rate. Thus, for the unirradiated sample, the recovery rate has been only 23% while for the samples with a 50% cross-linking rate, the recorded recovery rate was 100%.

The dependence between the heat-shrinking time and the cross-linking rate has been studied on samples with cross-linking rates

between 18 up to 50% and the shrinkage performed at 140° celsius on an item limiting this rate at 50%. Figure 5 shows the results obtained with this sample. One can notice a sharp drop of the heat-shrinkage time versus the cross-linking time. We found that other factors such as shrinkage temperature and the additives' chemistry also play a role in this (Figure 6).

As this figure shows, the heat-shrinkage drops while the shrinkage temperature rises. On the other hand, the gap we noticed with those two tubes receptors concerning heat-shrinkage time might be related to the plastified quality of chlorparafine used as a fire retardant.

Figure 7 gives the heat-shrinkage force variation versus the cross-linking ratio with tubes drawn 2:1 and shrinkage 18.7%. Table 1 shows the values of the heat-shrinkage force versus the cross-linking rate when the shrinkage is made at an open flame, 140° celsius temperature, and also after a sudden cooling at 20° celsius. The data analysis indicates that the heat-shrinkage force grows exponentially with the cross-linking rate at both high temperatures and room temperature. On the other hand, one notices that the heat-shrinkage force varies very little with the temperature when the sample has a higher temperature than the vitrifying point and grows considerably at the cooling time.

Several measurements have shown that the heat-shrinkage force diminishes while the shrinkage rate grows (Figure 8). Thus, it appears that strong heat-shrinkage forces are obtainable at a small level of shrinkage rate as well as at a cross-linking rate of about 60%. However, it must be mentioned that when the cross-linking rate surpasses the value of 65-70%, the tubes cannot be drawn any more.

A series of experiments were aimed to study the influence of factors, such as temperature, ultra-violet and ionizing radiation fields on the memory of heat-shrinkable tubes. Thus, it has

been found that by keeping some heat-shrinkable tubes for 24 hours at 40° celsius, the shrinkage rate remains the same. Intense fields such as ultra-violet and ionizing radiation, though, lead to the loss of heat-shrinkable tubes' memory, as a result of some processes of the polymer's molecular rearrangement during the drawing. New cross-linkings appear preventing the material's relaxation.

The heat-shrinkable items obtained have been analyzed also regarding their electrical and mechanical features (Table 2); and by comparing our data with those given to us by foreign firms producing heat-shrinkable tubes, one can draw the conclusion that the domestic production output is quite competitive.

Using these items in the electronic and electrotechnical fields brings important technical and economical advantages. Being flexible and highly safe in operation, the heat-shrinkable tubes have many uses to insulate and encapsulate electric connections between the conductors and their terminals (connectors).

Modern wiring systems using heat-shrinkable tubes for joints confer less cumbersome electrical insulation due to the small diameter tubes which further shrink, encapsulating the joints and the connectors. These systems also protect against steam and other corrosive media.

Compared with classic joining systems, the new procedure is an outstanding improvement in technical development.

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Lucrare în redacție: 5. V. 1982

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Translated from the technical Magazine: "The Plastic Materials"2, 1983

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